Calculating the freely dissolved chemical concentration from measured total or dissolved concentrations

$$\phi = \frac{C_{free}}{C_{total}} \quad (1)$$

$$C_{total} = C_{free} + C_{doc} + C_{poc} \quad (2)$$

$$\phi = \frac{1}{(1 + \chi_{POC} \cdot 0.35 \cdot K_{OW} + \chi_{DOC} \cdot 0.1 \cdot 0.35 \cdot K_{OW})} \quad (3)$$

$$C_{free} = \frac{C_{doc}}{(1 + \chi_{DOC} \cdot 0.1 \cdot 0.35 \cdot K_{OW})} = \frac{C_{doc}}{(1 + \chi_{DOC} \cdot K_{OC})} \quad (4)$$

where:

ϕ	Fraction of freely dissolved chemical in water (bioavailable solute fraction)
C_{total}	Total chemical in water (pg/L); unfiltered water concentration
C_{free}	Freely dissolved chemical in water (pg/L); chemical not associated with either dissolved or particulate organic material
C_{doc}	Chemical in water associated with DOC
C_{poc}	Chemical in water associated with POC
χ_{POC}	Concentration of particulate organic carbon in the water (kg/L); POC is the particulate organic matter content, that which passes through a 1 μm filter.
χ_{DOC}	Concentration of dissolved organic carbon in the water (kg/L); DOC is the dissolved organic carbon content, that which passes through a 0.45 μm glass fiber filter
0.35	Proportionality constant; this reflects the absorbing capacity of particulate organic carbon (POC) compared to octanol (or, more generally, the degree that OC mimics partitioning property of octanol).
0.1	Partitioning properties of DOC relative to POC; where (0.1) × (0.35) reflects the reduced absorbing capacity of dissolved organic carbon (DOC) compared to octanol. Burkhard (2000) recommends a value of 0.08, rather than 0.035. Note that for the organic carbon-water partition coefficient: $K_{OC} \cong (K_{OW}) \times (0.08)$.

After the fraction associated with POC is removed by filtering, "dissolved" means the fraction associated with DOC plus whatever is freely dissolved. The fraction associated with DOC can then be "removed" through calculation, to give the freely dissolved concentration using equation (4).

		Case 1	Case 2
Octanol-water partition coefficient	K_{OW}	6.67	6.67
Particulate OC concentration in water	χ_{POC}	1.26E-06	
POC proportionality constant	---	0.35	
Dissolved OC concentration in water	χ_{DOC}	1.60E-06	1.60E-06
DOC proportionality constant	---	0.080	0.080
Bioavailable solute fraction	ϕ	0.273	0.626
C_{doc} (measured)			4.35
C_{total} (measured)		15.08	
C_{free} (estimated)		4.12	2.72

If you start with C_{total}, and use the full POC/DOC equation (1) - Case 1 above - the estimate of C_{free} is 4.12. However, if you start with C_{doc}, and use the DOC-only equation (4) - Case 2 above - the estimate of C_{free} is 2.72 or about 51% less. Case 2 assumes (as does Morrison et al., 1997) that all of the chemical associated with POC was removed by filtering.